Degradation of Organic Contaminants in Water by Solar Radiation: Examining the Photochemical Transformation Pathways of 2,4-Dimethylphenol in the Presence of Dissolved Organic Matter

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Abstract

Produced water is the greatest source of waste by product associated with oil and natural gas operations. This study, examined the potential for solar radiation to effectively degrade toxic organic compounds commonly found in produced water, specifically 2,4-dimethylphenol (DMP). Treatment of these contaminants by solar irradiance is an attractive treatment alternative, as harnessing the sun's light energy is a "green" approach that could be an economical and effective means to remediate produced water. Direct and indirect photolysis experiments were conducted at concentrations found in "treated" produced water, using pH adjusted reaction solutions with respect to environmental fresh water systems (pH≈8). Further the effect of dissolved organic matter (DOM) as a "photosensitizer" (catalyst) was investigated. Analysis of direct and indirect photolysis experiments by high-pressure liquid chromatography (HPLC) with detection by UV absorption at 272nm revealed photodegradation that obeyed first order kinetics. Indirect photolysis experiments in the presence of DOM utilized Suwannee River Fulvic Acid (SRFA), a terrestrially derived DOM and Pony Lake, Antarctica Fulvic Acid (PLFA) a DOM derived from algal precursors. Reactions solutions were prepared at environmentally relative total organic carbon concentrations (TOC≈3-5mg/L). Both DOM mediated DMP photolysis occurred at increased rates relative to direct photolysis, but was significantly faster in reactions involving SRFA. To determine the indirect pathways of degradation, molecular probes were used as competitive scavengers that reacted with specific reactive

phototransients e.g. radicals, reactive oxygen species, etc. It was concluded that DMP degrades by reaction with photo-excited triplet DOM (^{3}DOM). Overall, it has been shown that the organic contaminant DMP photodegrades significantly in the presence of DOM and sunlight.

Acknowledgements

I would like to thank Yo Chin for steering me towards geology, taking me on as a student, and giving me all the opportunities one could hope for. Many thanks to all Chin members present and past that have contributed to my growth as a scientist. Special thanks to Collin Ward and Marcy Card for their guidance. To my fellow Ohio State geologists, thanks for the memorable trips and experiences.

Introduction

Oil and natural gas reservoirs have a natural boundary between hydrocarbons and groundwater known as the formation layer. As the oil and gas level drops in a well, additional water is injected into the geological media in order to pump out the overlying hydrocarbons. The volume of water injected significantly increases when removing hydrocarbons from an aging well. This "produced water", mixes with the hydrocarbons and is brought to the surface during production. On the surface, produced water is separated, treated, and then either discharged into surrounding surface waters or into a holding reservoir [1]. Produced water is a serious consequence of our dependence upon fossil fuels. At present, treated produced water often have unacceptable levels of organic contaminants e.g. anthracene, benzo(a)pyrene, naphthalene, xylenes, etc. Current practiced methods include gravity-based separation and micro-filtration, which are both costly and focus on removing insoluble contaminants with little attention paid to dissolved organics.

One of the substances that remain after the treatment process is 2,4-dimethylphenol. Because many organic pollutants are not removed in treated produced water, further treatment may be needed. One option is to harness sunlight as an effective and economical means to remediate produced water. Sunlight might be a viable option to break down harmful organic contaminants, due to 1) the potential existence of light-absorbing chromophores associated with the structure of a compound and 2) the ability to produce photosensitizers in the presence of dissolved organic matter (DOM).

Thus, *I propose that solar radiation has the potential to effectively degrade toxic organic compounds found in produced water, specifically 2,4-dimethylphenol (DMP), commonly found in produced waters.* DMP is an aromatic hydrocarbon classified by the UN as a poisonous substance and a marine pollutant [2]. High concentrations of DMP (≈2.5μM) have been reported after standard treatments of produced water [1]. To date, little research has explored the photochemical transformation pathways of this contaminant. Since produced water is released into surrounding natural environments, contaminants associated with this waste can enter aquatic surface waters and interact with constituents of those waters. It is well known that dissolved organic matter (DOM), an amorphous mixture, derived from decaying terrestrial and microbial material, is ubiquitous to all surface waters, is photochemically active and can affect transformation of contaminants through the photolytic production of reactive species and intermediates [3]. Understanding how DMP reacts with DOM in the presence of sunlight will help shed light on photochemical pathways of its degradation and its ultimate environmental fate.

Project Objectives

I hypothesize that DMP will degrade through photolysis, and that transformation will be enhanced in the presence of dissolved organic matter. I hope to show that photodegradation is a viable technique for treating this and similar organic contaminants in produced water.

The three objectives of this project are to:

(1) assess the photodegradation of DMP,

(2) evaluate the photofate of DMP in the presence of dissolved organic matter, and

(3) determine indirect pathways responsible for the photodegradation of DMP.

Experimental Methods and Procedures

Assessing Photodegradation of DMP:

Experiments by direct photolysis (in water only) were performed to determine the kinetic order of reaction and photodegradation rate coefficient of (DMP). Reaction solutions were made using relevant initial concentrations of DMP (≈2-3μM) found in produced water. Solutions were made in ultrapure Milli-Q water and pH adjusted with respect to environmental fresh water systems (pH ≈ 8). These experiments were conducted using a solar simulator (Atlas Suntest CPS+), which simulates the radiation of the sun using a 450W Xenon arc lamp and appropriate filters that screen out wavelengths not present in natural sunlight. Quartz tubes, which transmit both UV and visible light, were filled with solutions of the analyte. These quartz reaction tubes were sealed with Teflon tape wrapped O-rings and clamped shut. The reaction tubes were then placed in the Suntest and removed at specific time points for DMP analysis in order to determine the degradation rates. Dark controls were wrapped in aluminum foil and placed along side tubes in the Suntest. Samples were irradiated over multiple half-lives to determine the order of kinetics. Irradiance of the Suntest was tested for consistency using a radiometer as well as chemical actinometers p-nitroanisole and pyridine [4]. Solutions were then assayed using reverse-phase high-pressure liquid chromatography (HPLC)

coupled with UV-Vis detection to determine concentrations of DMP. The specific method for detecting DMP on the HPLC was developed using a Cary UV-Vis spectrophotometer to measure an absorption spectrum to determine the optimum wavelength for detection. Various mobile phase compositions were tested to determine the optimum separation of peaks on the HPLC. DMP was monitored at 272nm and the mobile phase consisted of a 50:50 solution of water and the organic solvent acetonitrile. A calibration curve was developed with every new solution of mobile phase using multiple standard concentrations of DMP. A kinetics curve was then constructed determining the reaction order and observed rate coefficient to elucidate the phototransformation of DMP by direct photolysis.

Assessing the interaction of DOM on DMP Photolysis:

The introduction of DOM, an important photosensitizer ubiquitous to all waters, has the potential to greatly enhance the degradation of DMP. DOM in the presence of sunlight is known to indirectly increase the photoreactivity of many organic compounds, through the formation of reactive oxygen species (ROS) such as the hydroxyl radical (OH•), as well as through excited singlet and triplet state DOM pathways [3,5], which can subsequently reacts with the contaminants of interest. Solutions of DMP and DOM were made at an environmentally relevant carbon concentration (≈3-5mg/L) and identical experimental parameters were performed as mentioned above. Total organic carbon analysis was measured on a Shimadzu TOC-5000 carbon analyzer, thereby determining the exact amount of carbon available in the reaction. The

kinetics associated with this experiment assessed DOM's indirect influence on the photodegradation compensate pathways of DMP. Both microbially-derived Pony Lake, Fulvic Acid (PLFA) and a terrestrially-derived Suwannee River, Fulvic Acid (SRFA) International Humic Substance Society (IHSS) reference samples of a DOM isolate were used in order to determine differences in reactivity due to varying composition of DOM. Experiments involving SRFA solutions were conducted at 5.82 ± 0.005 mg of carbon/L and PLFA solutions were conducted at 3.48 ± 0.014 mg of carbon/L.

Determining the contributions of indirect photolytic pathways to DMP degradation:

In order to elucidate indirect pathways, molecular probes were used as competitive scavengers to assess the reactivity of specific photosensitizers, specifically the ROS, singlet oxygen ($^1O_2$), other ROS and triplet DOM (^{3}DOM). A decrease in reactivity of DMP involving the introduction of a scavenger molecule would indicate a distinguishable pathway of transformation. Isopropanol is known to react readily with ROS, such as hydroxyl radical (OH•), peroxyl radical (ROO•), and oxyl radical (RO•) [6]. DMP solutions were prepared in both PLFA and SRFA with 25mM isopropanol to determine the contribution of ROS pathways. The azide anion (N^{3-}) is highly specific quencher for $^1O_2$ [7]. An experiment was conducted involving DMP in SRFA with 2mM sodium azide to investigate the role of $^1O_2$. Recent studies have shown that DOM mediated photolysis of 2,4,6-trimethylphenol (TMP) degrades significantly through direct reaction with photo-excited ^{3}DOM [8,9]. Further,

reactions involving OH• and $^1O_2$ with TMP are believed to be negligible [9]. DMP and TMP are alkylphenols, differentiated by an additional methyl group substitution on the conjugated ring of TMP. The methyl groups serve as electron donors in the photo-oxidation of TMP [8]. I postulated that the dominating pathway associated with TMP is of equal or greater importance with regard to the photoreactivity of DMP. Therefore, an experiment was set up involving DMP in SRFA with 10μM TMP in order to assess the significance of the suspected pathway, ^{3}DOM.

Discussion/Results

DMP was assayed by means of triple injections on the HPLC. Dark controls retained initial concentrations (2-3μM) throughout all experiments, verifying that irradiation initiates the reactions. Consistent temperature (ranges: 14.1 – 23.2 °C) and radiometer readings (ranges: 2.80 – 3.22 W/cm^2) were recorded as well. Analysis of the rate data reveal that first order kinetics was obeyed, and I was able to measure both rate constants and half-lives (refer to appropriate figures and tables). I observed enhanced DMP photodegradation in the presence of PLFA (≈ 1.8x) (Figures 2 – A,B) and more significantly with the addition of SRFA (≈ 9.1x) (Figures 3 – A,B). Upon examining Figure 4, we see a clear difference in rates, as the allochthonous material reacts far more readily then the autochthonous counterpart. This is in contrast to data observed by others with respect to the photodegradation of 2,4,6-trimethylphenol, as DOM with a greater autochthonous composition was shown to be more photo-reactive [10,11,8]. DOM from a eutrophic

environment has been show to react readily with photo-excited ^{3}DOM [8]. Therefore, my observations that show the greatest reactivity in SRFA suggests that another mechanism, other than the suspected pathway (^{3}DOM), contributes to the photofate of DMP. While the isopropanol experiments (strong OH• quencher, weaker ROO• quencher) showed that ROS were not contributing pathways, peroxyl radical could be a potential mechanism. It has been shown that ROO• can be an important mechanism at low concentrations of 2,4,6-trimethylphenol, (TMP<5μM) [10]. The experiments conducted in this study were within this concentration range, therefore future anoxic experiments should be done to elucidate the contributions of ROO• and other ROS.

In the presence of 25mM isopropanol, degradation rates remained unchanged in PLFA (Figure 5 – A) and in SRFA (Figure 5 – B). Hence, the role of ROS, most notably OH•, is insignificant. My data corroborates observations made by others with respect TMP, which have shown that the hydroxyl radical does not play a significant role in the photo-oxidation of electron-rich phenols [12,10,8].

The addition of 2mM azide anion (N^{3-}) to SRFA (Figure 6), a known singlet oxygen scavenger, did not produce quenching results thereby eliminating $^1O_2$ as a pathway. This is in contrast to the findings by Faust and Hoigne [13], who detailed that singlet oxygen plays a minor role in the photofate of TMP. However, my results corroborate studies made by Canonica et al., [9] and Cawley et al., [8], which have shown that singlet oxygen is not a

significant contributing pathway in the photo-oxidation of TMP. Further this data strengthens the argument that structurally similar DMP and TMP breakdown through analogous mechanisms.

2,4,6-trimethylphenol (TMP-10μM) was added at 4x the concentration of 2,4-dimethylphenol (DMP-2.5μM). The presence of TMP did not change the photodegradation rate for DMP (Figure 7 – A). However, TMP reacted **more than 2x faster** than DMP (Figure 7 - B). Studies have shown that alkylphenols exhibit enhanced photoreactivity with increasing ring substitutions by electron-donating methyl groups [13]. This investigation corroborates the work previously mentioned, as the observed reaction rates increased with respect to the number of methyl groups associated with TMP and DMP. Further, we suspect that there was an insufficient amount of TMP added to compete with DMP for ^{3}DOM as both were highly reactive (Figure 8).

Conclusion

To date, little research has been conducted involving the photofate of 2,4-dimethylyphenol. DMP is suspected to react readily with the phototransient ^{3}DOM. Photo-initiated oxidation of DMP is believed to occur through excited ^{3}DOM as the two methyl groups take part in electron transfer reactions that stabilize the conjugated ring, allowing for DMP to form a stable cation. As observed with TMP, scavenging experiments associated with isopropanol and azide anion reveal that ROS and $^1O_2$ contributed insignificantly to the photofate of DMP. Therefore, with respect to the observed quenching experiment results and the known photoreactivity of the molecular probe TMP, we conclude that

photo-excited triplet DOM is the critical indirect photodegradation pathway along with another unidentifiified photo-reactive transient. The research shows that solar radiation coupled with DOM quickly degrades DMP and could be an inexpensive technology to treat alkyl phenol contaminated produced water.

A possible treatment method would include constructing a wetland to treat organic contaminants in produced water. The wetland would need to be shallow so that sunlight could penetrate easily and the water could be mixed thoroughly. Also, there would need to be specific higher plant material to allow constant DOC input. Further the constructed wetland would need to be close to the site of operations in order for continual cyclic treatments and to keep transportation costs low.

Recommendations for Future Work

To investigate this matter further, two experiments should be conducted involving (1) the photodegradation of DMP in the presence of DOM and natural sunlight and (2) the photoreactivity of DMP and DOM in a sample of produced water. Examining the photofate of DMP in natural sunlight will assay the reactivity that would occur in an environmental setting. Assessing the reactions rates of DMP in produced water will shed light on the feasibility of the proposed technique.

References

1. Veil, J.A., Puder, M.G., Elcock, D., and R.J. Redweik, Jr. 2004. A White Paper Describing Produced Water from Production of Crude Oil, Natural Gas, and Coal Bed Methane, prepared by Argonne National Laboratory for the U.S. Department of Energy, National Energy Technology Laboratory.

2. International Programme on Chemical Saftey, 2003, 2,4-Dimethylphenol Hazard Data Web: http://www.inchem.org/documents/icsc/icsc/eics0458.htm (accessed 5/10/10)

3. Miller, P.L. and Y.P. Chin. 2005. Indirect photolysis promoted by natural and engineered wetland water constituents: Processes leading to alachlor degradation. *Environ. Sci. Technol.*

4. Dulin, D. and T. Mill. 1982. Development and evaluation of sunlight actinometers. *Environ. Sci. Technol.*

5. Jacobs, L.E., Weavers, L.K., and Y.P. Chin. 2008. Direct and indirect photolysis of polycyclic aromatic hydrocarbons in nitrate-rich surface waters. *Environ. Toxi. and Chem.*

6. Sugita, M., Yatsuhashi, T., Shimada, T., and H. Inoue. 2001. Chemical behavior of oxygen-radical: quenching process of cumyloxyl radical by nicotinamide derivatives. *Journal of Photochemistry and Photobiology A: Chemistry*

7. Gerecke, A.C., Canonica, S., Muller, S.R., Scharer M., and R.P. Schwarzenbach. 2001. Quantification of Dissolved Natural Organic Matter (DOM) Mediated Phototransformation of Phenylurea Herbicides in Lakes. *Environ. Sci. Technol.*

8. Cawley, K.M., Hakala, J.A., and Y.P. Chin. 2009. Evaluating the triplet state photoreactivity of dissolved organic matter isolated by chromatography and ultrafiltration using an alkylphenol probe molecule. *Limnol. Oceanogr. : Methods*

9. Canonica, S., and J. Hoigne, 1995. Enhanced oxidation of methoxy phenols at micromolar concentration photosensitized by dissolved natural organic material. *Chemosphere*

10. Canonica, S., and M. Freiburghaus. 2001. Electron-rich phenols for probing the photochemical reactivity of freshwaters. Environ.Sci. Technol. 35:690-695.

11. Richard, C., O. Trubetskaya, O. Trubetskoj, O. Reznikova, G. Afanaseva, J. P. Aguer, and G. Guyot. 2004. Key role of the low molecular size fraction of soil humic acids for fluorescence and photoinductive activity. Environ. Sci. Technol. 38:2052-2057.

12. Allen, J. M., and B. C. Faust. 1994. Aqueous-phase photochemical formation of peroxyl radicals and singlet molecular oxygen in cloud water samples from across the United States, In: Aquatic and Surface Photochemistry, G. R. Helz, R. G. Zepp, and D. G. Crosby, Editors. Lewis, p. 231-239.

13. Faust, B.C., and Hoigne, J., 1987. Sensitized Photooxidation of Phenols by Fulvic Acid in Natural Waters. *Environ. Sci. Technol.*

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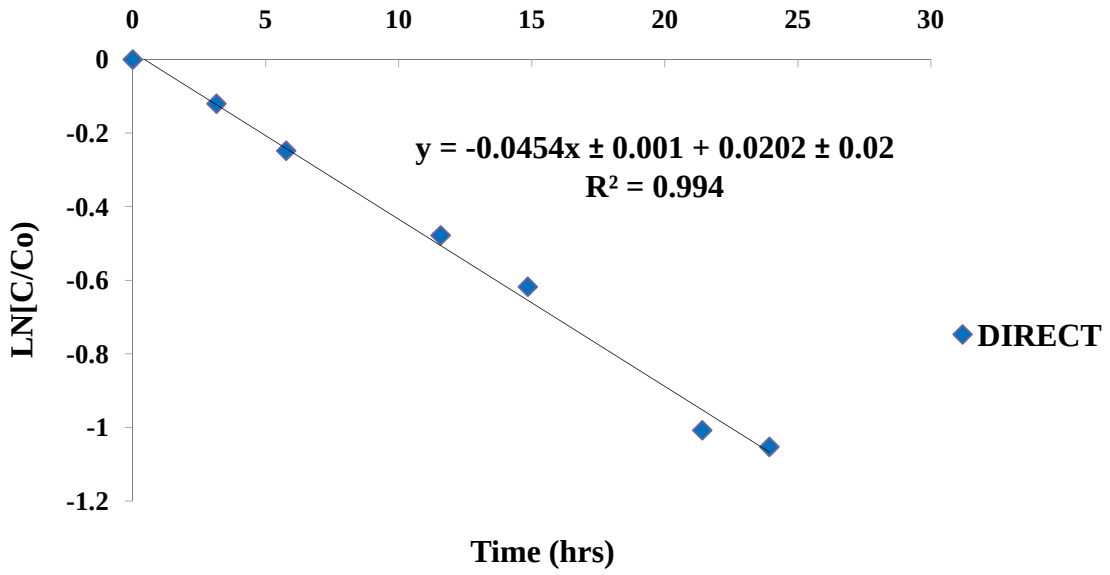

Figure 1: Direct photolysis of DMP

Table: 1	Direct
k (hrs^{-1})	0.0454 ± 0.001
t½ (hrs)	15.3

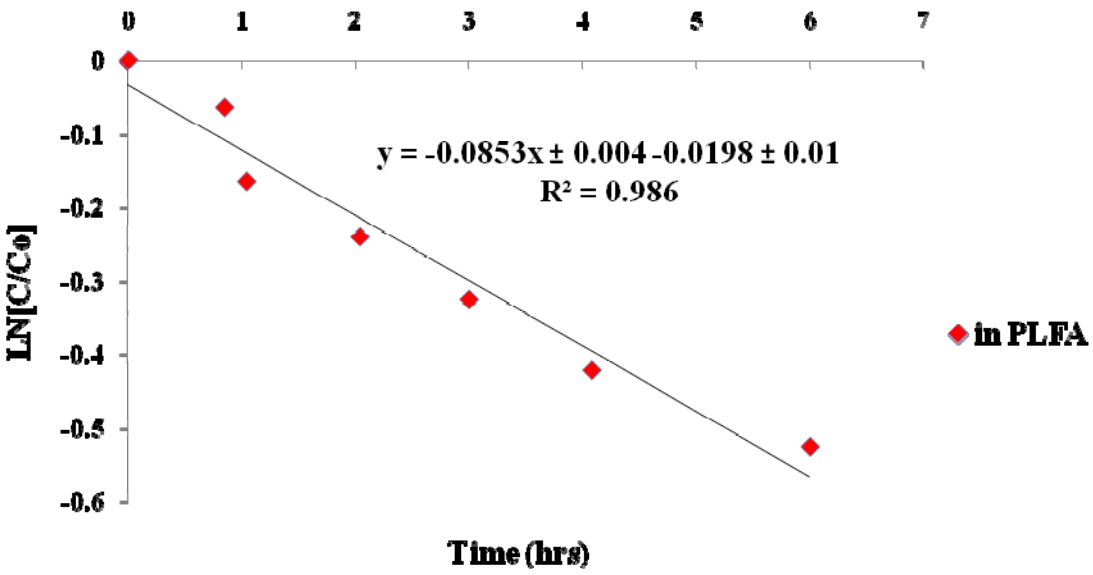

Figure 2-A: Indirect photolysis of DMP in PLFA

Table 2 – A	in PLFA
k (hrs^{-1})	0.0853 ± 0.004
t½ (hrs)	8.13

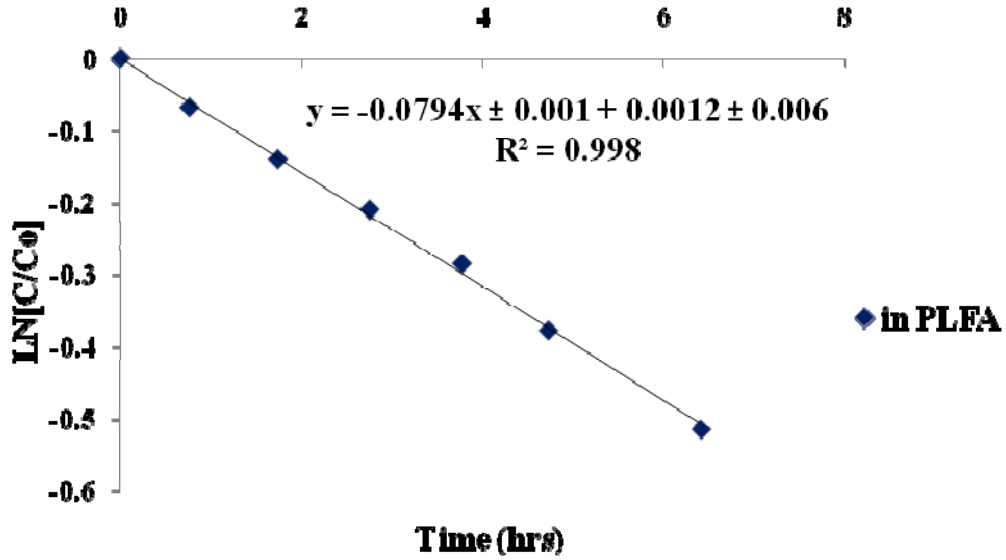

Figure 2-B: Indirect photolysis of DMP in PLFA

Table 2 – B	in PLFA
k (hrs^{-1})	0.0794 ± 0.001
t½ (hrs)	8.73

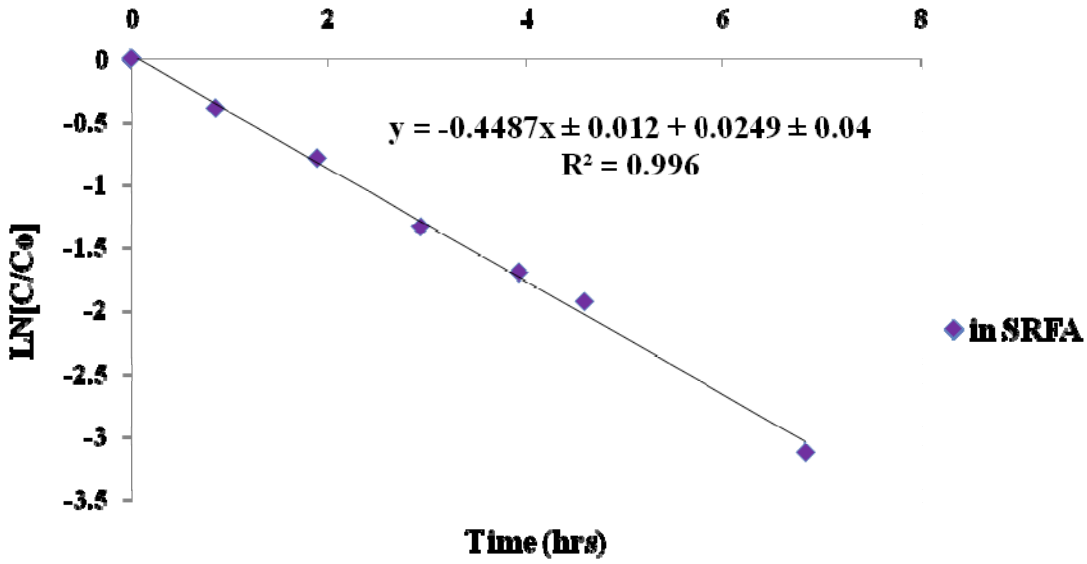

Figure 3-A: Indirect photolysis of DMP in SRFA

Table 3-A	in SRFA
k (hrs^{-1})	0.4487 ± 0.012
t½ (hrs)	1.54

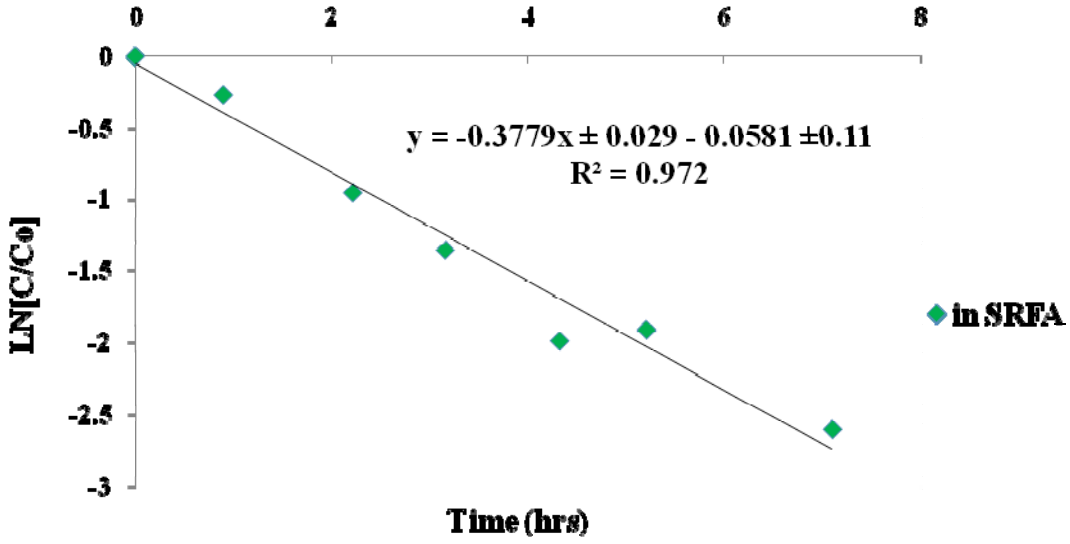

Figure 3-B: Indirect photolysis of DMP in SRFA

Table: 3b	in SRFA
k (hrs^{-1})	0.3779 ± 0.029
t½ (hrs)	1.83

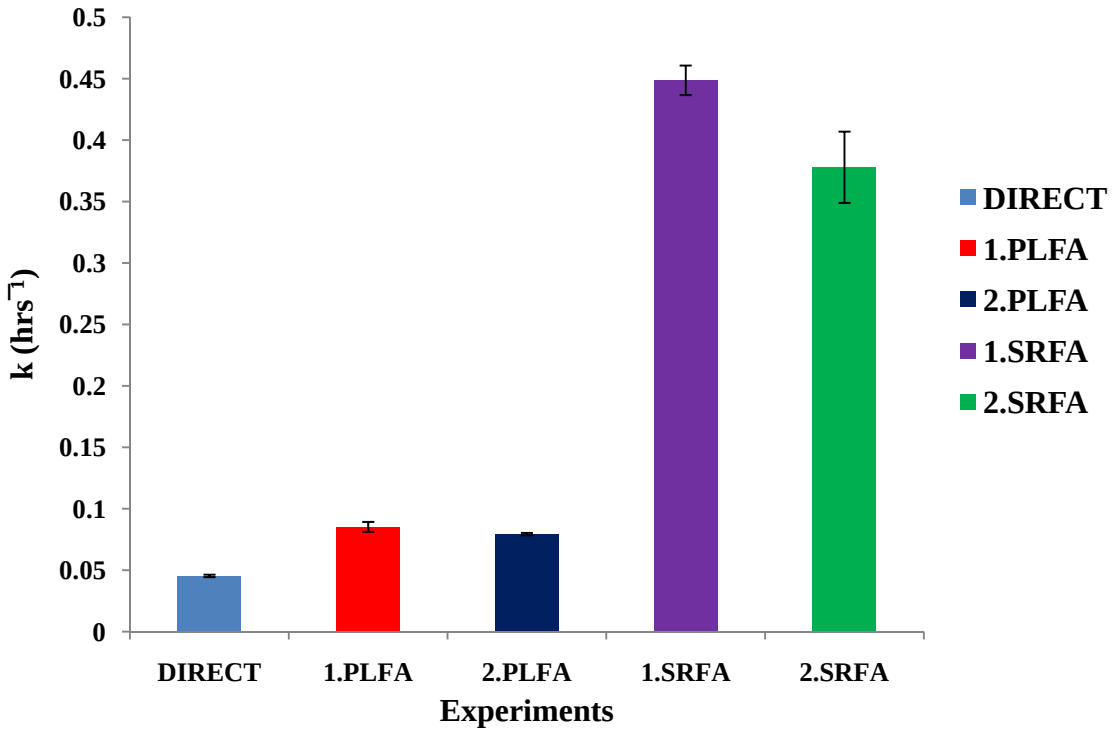

Figure 4: Degradation rate constant coefficients of direct and indirect experiments, error bars deduced from regression analysis of kinetic curves

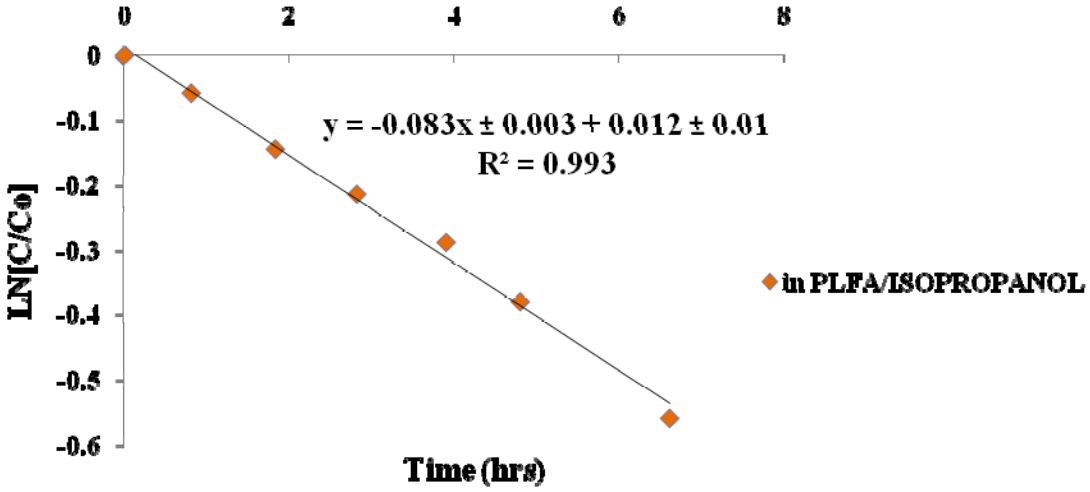

Figure 5-A: Indirect photolysis of DMP in PLFA and isopropanol

Table 5-A	in PLFA/ISOPROPANOL
k (hrs^{-1})	0.083 ± 0.003
t½ (hrs)	8.35

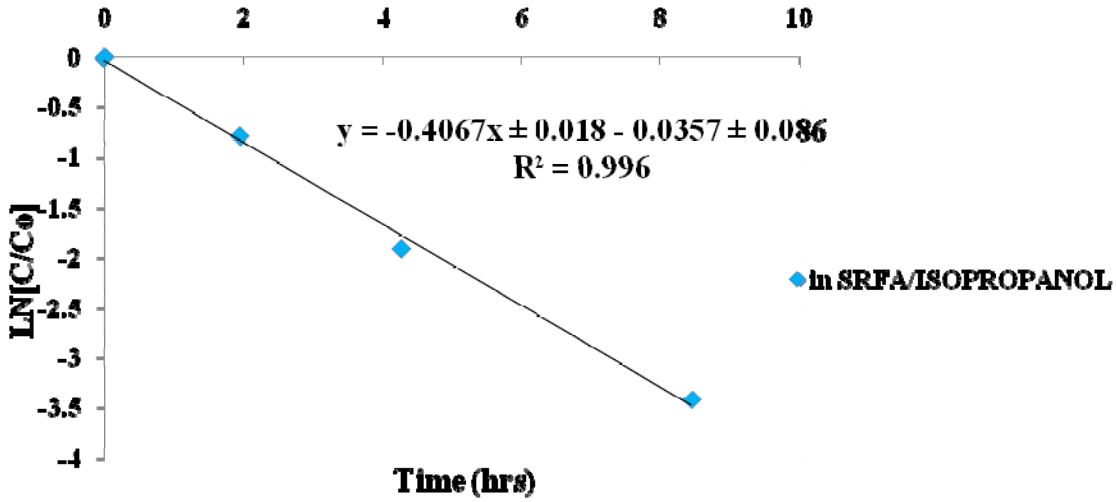

Figure 5-B: Indirect photolysis of DMP in SRFA and isopropanol

Table 5-B	in SRFA/ISOPROPANOL
k (hrs^{-1})	0.4067 ± 0.018
t½ (hrs)	1.70

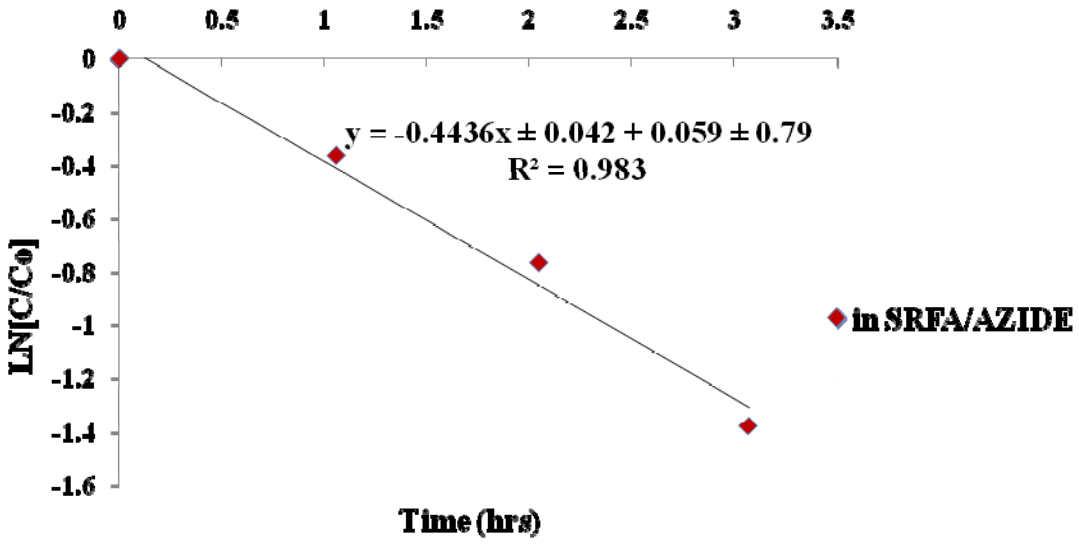

Figure 6: Indirect photolysis of DMP in SRFA and sodium azide

Table 6	in SRFA/AZIDE
k (hrs^{-1})	0.4436 ± 0.042
t½ (hrs)	1.56

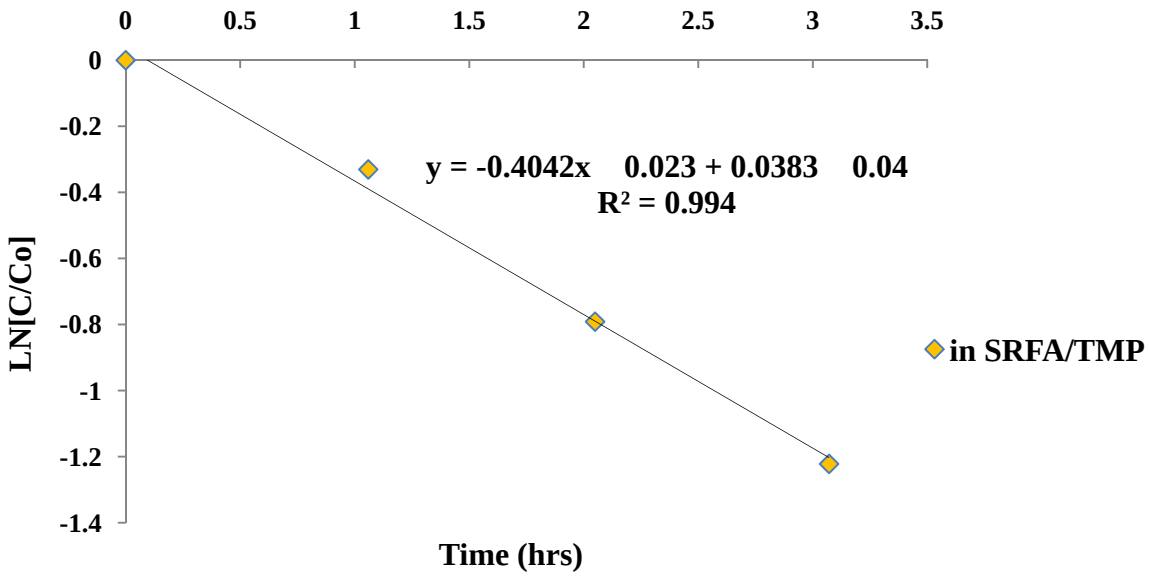

Figure 7-A: Indirect photolysis of DMP in SRFA and TMP

Table 7-A	in SRFA/TMP
k (hrs^{-1})	0.4042 ± 0.023
t½ (hrs)	1.71

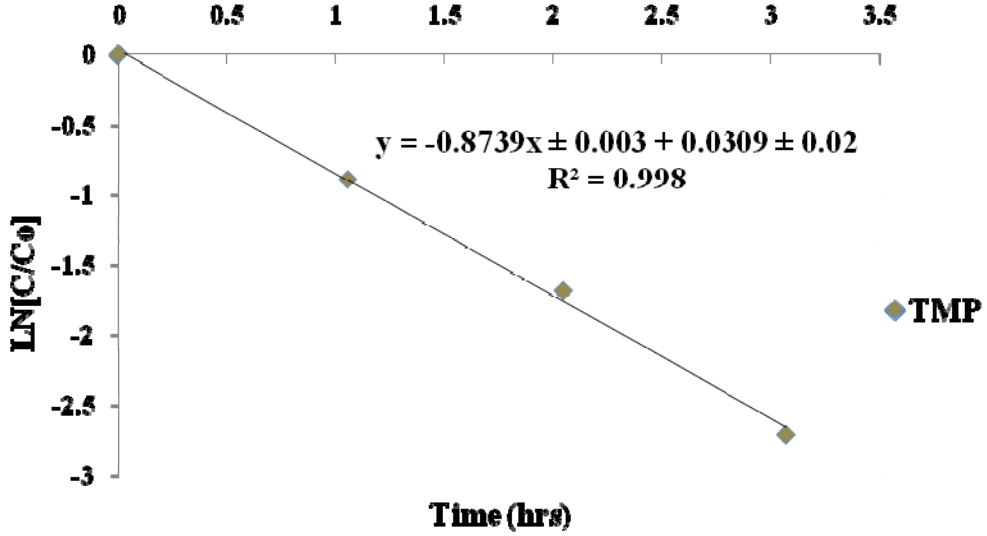

Figure 7 – B: Indirect photolysis of TMP in SRFA and DMP

Table 7-B	TMP
k (hrs^{-1})	0.8739 ± 0.003
t½ (hrs)	0.793

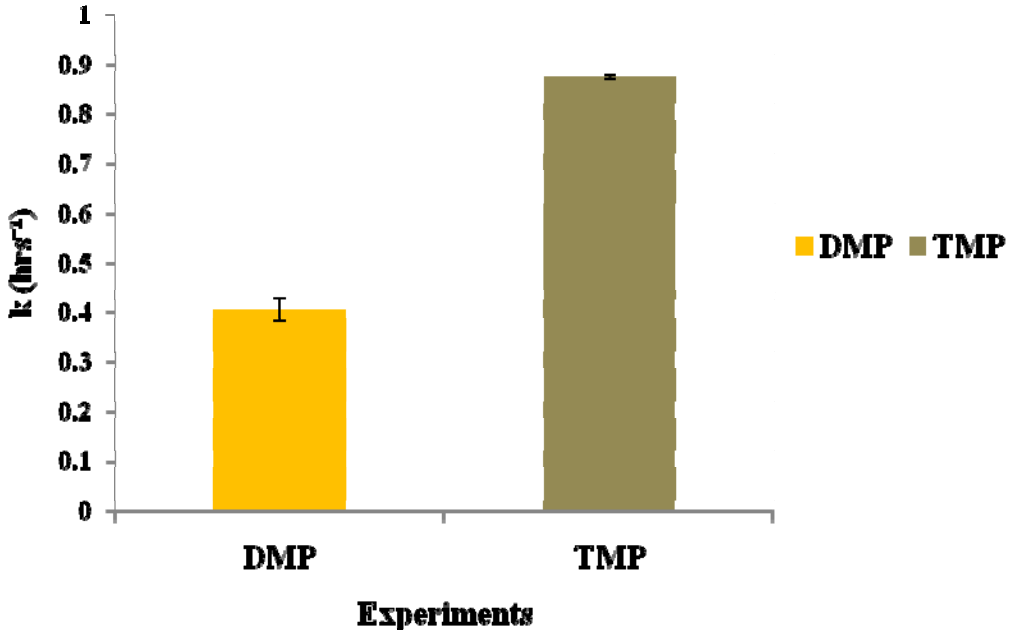

Figure 8: Degradation rate constant coefficients of DMP and TMP in SRFA, error bars deduced from regression analysis of kinetic curves